Fraunhofer Institut Angewandte Polymerforschung

Surface Research | pioneers in polymers

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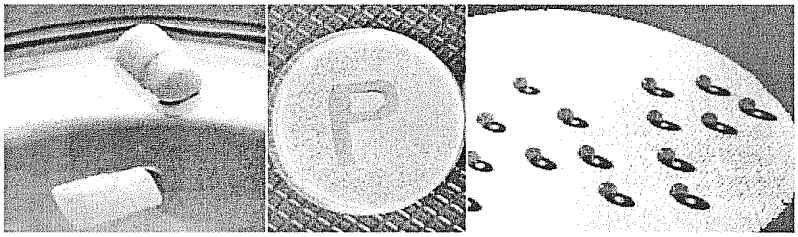
Polyelectrolyte layers



- Surface activation / oxidation of polymers
- Fluorine containing surface layers
- Atmospheric pressure DC glow discharge for polymer surface treatment
- Functionalized porous materials
- Adhesive free bonding
- Polyelectrolyte layers
- Plasma treatment of textiles
- Antimicrobial polymer surfaces
- Excimer treatment

Polyelectrolytes are polymers containing ionic groups on their backbones or on branches. They are mainly used because of their ion exchange properties.

There are different methods to produce thin layers of polyelectrolytes on surfaces of almost any bulk material. A lot of work was done on graft copolymerisation of olefinic ionic monomers onto polymers after introducing reactive sites as e.g. radicals or peroxides.

Another way to obtain polyelectrolyte layers is a direct plasma polymerisation process. It is possible to deposit ultrathin layers containing e.g. a high content of anionic functional groups from electron.cyclotron-resonance-microwave-plasmas. These layers are very homogeneous, stable and unsoluble in water.

Plasma Systems

- **Plasma reactors**
  The fundamentals of the polyelectrolyte layer deposition were investigated in a research plasma reactor.
  The results were used to scale the process to a semitechnical plasma reactor.

- **Monomers**
  As monomers for the plasma process, we use olefinic molecules with a high vapour pressure, e.g. acrylic acid. The deposition kinetics of these monomers as well as the properties of the resulting layers are well characterized (see list of publications).

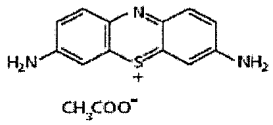
Layer Characterization

The characterization of the ionic plasma layers includes the detection of the volume

concentration of ionic groups within the layer via labeling of these functional groups with a cationic fluorescent dye as well as the investigation of the overall chemical constitution by infrared spectroscopy and electron spectroscopy for chemical analysis. Furthermore, an investigation of surface properties can be performed by contact angle goniometry and zeta potential measurements. Last but not least, .the determination of the physical appearance is possible via atomic force microscopy and electron microscopy.

- **Fluorecence labeling**
  The deposited layers are suspended in a solution of the cationic dye Thionine to stain all anionic groups with this cationic label. The dye can be removed from the layer by exchanging it in acid solution; the fluorescence intensity of this solution is a direct measure for the volume concentration of anionic groups in the plasma layer.
  It is possible to obtain polyelectrolyte layers containing up to 3e-4 mol/ccm ionic groups.

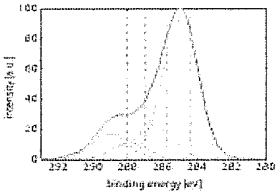
  Further information:
  Fluorecence labeling



Dye Thionine Acetate, CI52000 ($C_{12}H_9N_3S.C_2H_4O_2$). This dye is also known as Lauth´s Violett or Hoechst 33258.

- **X-ray photoelectron spectrometry**
  The high content of carboxylic ionic groups is confirmed by XPS.
  The total oxygen content of the plasma layers is 38%.

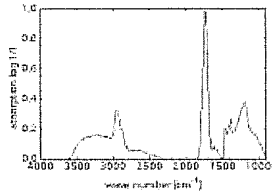
  Further information:
  X-ray photoelectron spectrometry (XPS)



X-Ray photoelectron spectrum of a Plasma Layer (Courtesy of W. Unger, Bundesanstalt für Materialforschung)

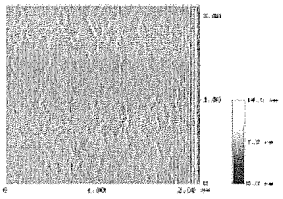
- **Infrared spectrometry**
  An Infrared spectrum of a carboxylic groups containing plasma layer reveals the expected peak abov 1700 cm^{-1} as well as the hydrogen bond signal between 3400 and 3000 cm^{-1}. Obviously, the layer is chemically quite heterogeneous, as can be seen from the fingerprintregion between 1400 and 900 cm^{-1}.

  Further information:
  Infrared spectrometry



IR spectrum of a Plasma Layer (Courtesy of M. Nitschke, Technische Universität Chemnitz-Zwickau)

- **Atomic force microscopy**
  A medium resolution AFM-investigation of the plasma layer reveals a pinhole-free, smooth surface. Experiments show that the surface flattens with increasing deposition time.



Surface of a Plasma Polymer on Polyethylene. The total surface area is 130µm x 130µm. (Courtesy of H. Kamusewitz, GKSS)

- **Contact angle goniometry**
  The carboxylic groups containing plasma layers have a relatively high surface energy of about 57 mJ/sqm. The water contact angle is 41°.

  Further information:
  Contact angle goniometry

- **Electron Microscopy**
  SEM images of cryobroken plasma layers on polyethylene give an idea of the density and

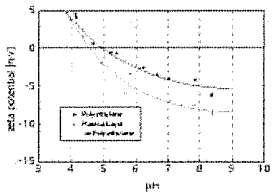
extent of crosslinking in comparison of the familiar structure of polyethylene.

Further information:
SEM on polymer-analysis.com

Plasma Polymer on Polyethylene. The yellow arrow points to the interface between Polyethylene and Plasma Layer. (Courtesy of A. Purz, IAP)

Zeta Potential

Compared to ethylene, the zeta potential of the plasma layers in 1e-3 mol KCl is - due to the ionic groups on the layer surface - higher. The isoelectrical point can be found at lower pH's.



Zeta potential of a Plasma Layer compared to Polyethylene. (Courtesy of K. Richau, GKSS)